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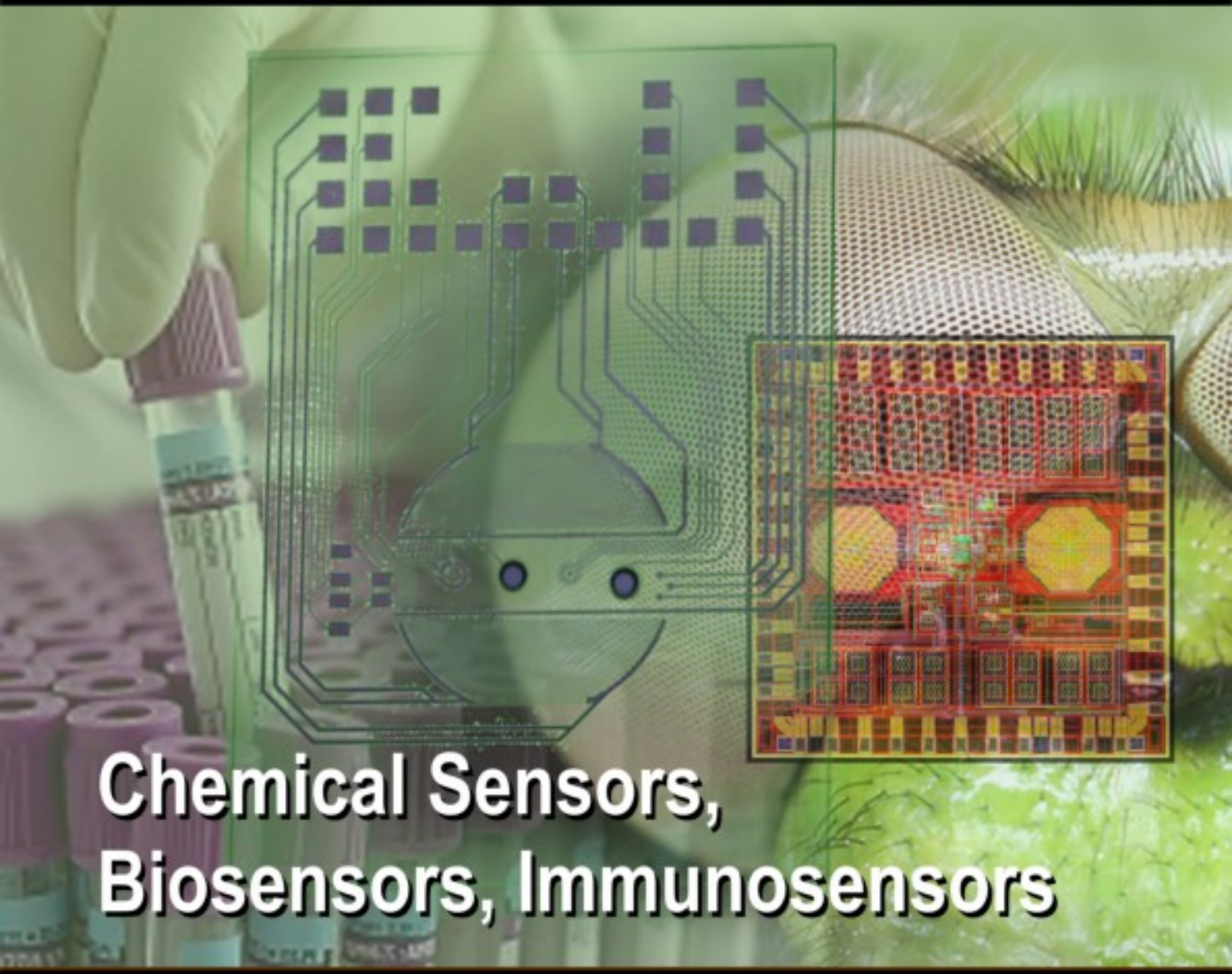

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Influence of Firing Temperature on Compositional and Structural Characteristics of ZrO_2 Thick Films Gas Sensor

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Abstract: In this paper, we explore for the first time the compositional, morphological and structural properties of the ZrO_2 thick films prepared by standard screen printing method and fired between 800 ^oC to 1000 ^oC for 2-hours in an air atmosphere. The material characterization was done by using XRD, X-ray energy dispersive analysis (EDAX), and scanning electron microscope (SEM). The deposited films were polycrystalline in nature. Also samples were found uniform and adherent to the alumina substrate. Effect of firing temperature on structural parameters such as grain size and surface area were calculated. The result indicates that grain growth can be increased by increasing firing temperature which is responsible for decreasing surface area. From the EDAX analysis it was found that the ZrO_2 films are non- stoichiometric in nature which is due to semiconducting behavior of the films. *Copyright © 2010 IFSA.*

Keywords: ZrO_2, Thick films, XRD, EDAX, SEM

1. Introduction

Zirconia is an important ceramic material; it is being widely used in catalysis, structural ceramics, thermal plasma spray technique etc., and is known for its thermal stability, resistance to thermal shock, suitable coefficient of thermal expansion and various other significant properties [1, 2]. ZrO_2 have been widely used for various applications such as semiconductor in dye-sensitized solar cell, catalysts,

fuel cells, resistors, gas sensors, transparent optical device, optical coating etc [3-5]. Several deposition methods have been used to grow undoped and doped ZrO_2 films such as Spray pyrolysis vacuum evaporation, chemical vapour deposition, Sol gel technique, Screen printing technique [6, 7]. Screen printing technique was introduced in the latter part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field. Screen printing is viable and economical method to produce thick films of various materials [8, 9] Semiconducting oxides are widely used as inexpensive and robust sensors for toxic, hazardous and combustible gases and vapors in safety and automotive applications. Few semiconducting oxide materials used in these applications are ZnO, SnO_2, Fe_2O_3, Cr_2O_3, TiO_2 and ZrO_2 etc [10-21].

The aim of the present work is to study structural properties of ZrO_2 thick films. Such a detailed understanding of the film properties is necessary if ZrO_2 is to be developed to a degree which will enable its use in gas or humidity sensing devices.

2 Experimental

Analar Reagent (AR) grade ZrO_2 powder was calcined at 400 ºC for 2 h in a muffle furnace. Then this powder was crushed and thoroughly mixed with a glass frit (PbO-70 %, SiO_2-18 %, Al_2O_3-9 % and B_2O_3-3 %) as a permanent binder. Organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose (EC) were added to this mixture to achieve proper thixotropic properties of the paste. The ratio of inorganic to organic parts was maintained at 70:30 (the ratio of active powder to permanent binder was kept at 95:5 in 70 % and the ratio of EC to BCA was 98:2 in 30 %). ZrO_2 thick films were prepared on alumina substrates using a standard screen-printing technique. The screen of nylon (40 s, mesh no.355) was selected for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen using a standard photolithography process. The paste was printed on clean alumina substrates (5 x 2 cm) with the help of a mask. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under infrared radiation for 45 minutes and fired at temperatures of 800, 900 and 1000 ^oC for 2 h (which includes the time required to achieve the peak firing temperature and then constant firing for 30 minutes at the peak temperature) in a muffle furnace. The structural properties of ZrO_2 films were investigated using X-ray diffraction analysis from 20-80^0 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) with CuKα, λ=0.1542 *nm* radiation] with a 0.1^o/step (2θ) at the rate of 2 s /step. A scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The composition of TiO_2 thick film samples were analyzed by an energy dispersive X ray spectrometer (EDS) (JOEL-JED 6360 LA). The thickness of the ZrO_2 thick films was measured using a Taylor-Hobson (Taly-stepUK) system. The thickness of the films was observed to be uniform in the range of 20 μm to 50 μm.

The crystallite size was determined using Scherer's formula [22].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \ , \tag{1}$$

where D is the crystallite size, λ is the wavelength of the X-ray radiation (1.542 Å), β is the peak full width half maxima of the (111) peak of the XRD pattern and θ is the diffraction angle.

The information about the crystalline shape and sizes of ZrO_2 thick film materials is obtained by using SEM [Model JOEL JED-2300(LA) Germany]. For SEM all the ZrO_2 samples were coated with a very thin conducting gold layer (few100Å) using vacuum evaporation/sputtering technique to avoid charging of the samples. The composition of ZrO_2 thick film samples were analyzed by Energy Dispersive Spectrometer (EDAX) (JOEL-JED 6360 LA).

Brunauer–Emmett–Teller (BET) method was applied for specific surface area evaluation and was calculated for spherical particles using the following equation [23].

$$Sw = 6 / \rho d, \quad (2)$$

where d is the diameter of the particles, ρ is the density of the particles.

3 Results and Discussion

3.3.1. Preheat Treatment

The preheat treatment for the material is necessary to decrease posterior materials instabilities. During this heat treatment the materials were submitted to high calcinations temperature to avoid instabilities during their working life. The calcinations of the powder before the paste preparation and the firing process of the printed film can determine the sensitivity of the active material layer. With calcinations, grain boundaries were developed and the powder sintered to bigger agglomerations. This causes a higher surface area after firing and attains higher sensitivity to the layer [24].

A drying stage is required to remove the organic solvents, make the printed film adhere to the substrate and be relatively immune to smudging. After printing, the film was allowed to settle in air for a few minutes so that some of the volatile solvents were evaporated slowly at room temperature. The organic agent was still present in the paste at this stage. Drying took place at temperatures between 70-180 ^{0}C either in a conventional oven or by placing films under infrared radiation [24].

The high temperature firing cycle is designed to remove the remaining organic binders, to develop the structural and electrical properties of the film and to bond the film to the substrate. Temperatures up to 1000 ^{0}C are required to achieve these objectives. During this firing process the glass frit melts and grains of the functional materials are held together and also the film becomes bonded firmly to the substrate. There are three distinct regions in this firing cycle. Firstly the temperature slowly was increased towards the peak firing temperature. During this time the remaining organics were removed. This occurred at 350-400 ^{0}C.As the temperature reached 600-1000 ^{0}C, the glass frit softens. Secondly the temperature remained constant for about 30 minutes. During this time the active material sintered and various reactions took place. The electrical properties of the film began to develop. Finally there was a cooling stage to room temperature that allows the glass frit to solidify [24]. Softening point of glass frit is in between the temperature range 500-700 ^{0}C [25]. Hence the minimum and maximum firing temperature range was selected 800 ^{0}C to 1000 ^{0}C respectively.

3.3.2. Elemental Analysis

Table 1 shows the composition of the films fired at different temperatures. The EDS spectrum showed the presence of only Zr and Oxygen. From the analysis it was found that the ZrO_2 films are non-stoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity. Zirconium oxide looses oxygen on heating so that Zr is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess Zr ions in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the n-type semiconductor [26, 27]. The EDAX results show lot of variation Zr/O ratio with firing temperature.

Table 1. Composition of ZrO_2 obtained from EDAX.

Element (Mass %)	Firing Temperature		
	800 ºC	**900 ºC**	**1000 ºC**
Zr	79.10 %	82.14 %	82.04 %
O	20.90 %	17.86 %	17.96 %

The mass % of Zr and O in each sample was not as per the stoichiometric proportion and all samples were observed to be oxygen deficient. It is very important for gas sensing applications. Excess or deficiency of the constituent material particles leads to the semiconducting nature of the material. It is found that high value of Zr/O ratio for ZrO_2 film is at 900 ^{0}C firing temperature. Therefore the ZrO_2 thick film with optimized firing temperature of 900 ^{0}C is chosen for further studies of pure ZrO_2 samples.

3.3.3. Structural Parameters and their Analysis

Fig. 1 shows X-ray diffraction patterns obtained for ZrO_2 thick films deposited on alumina substrates and fired at 800, 900 and 1000 ^{0}C.

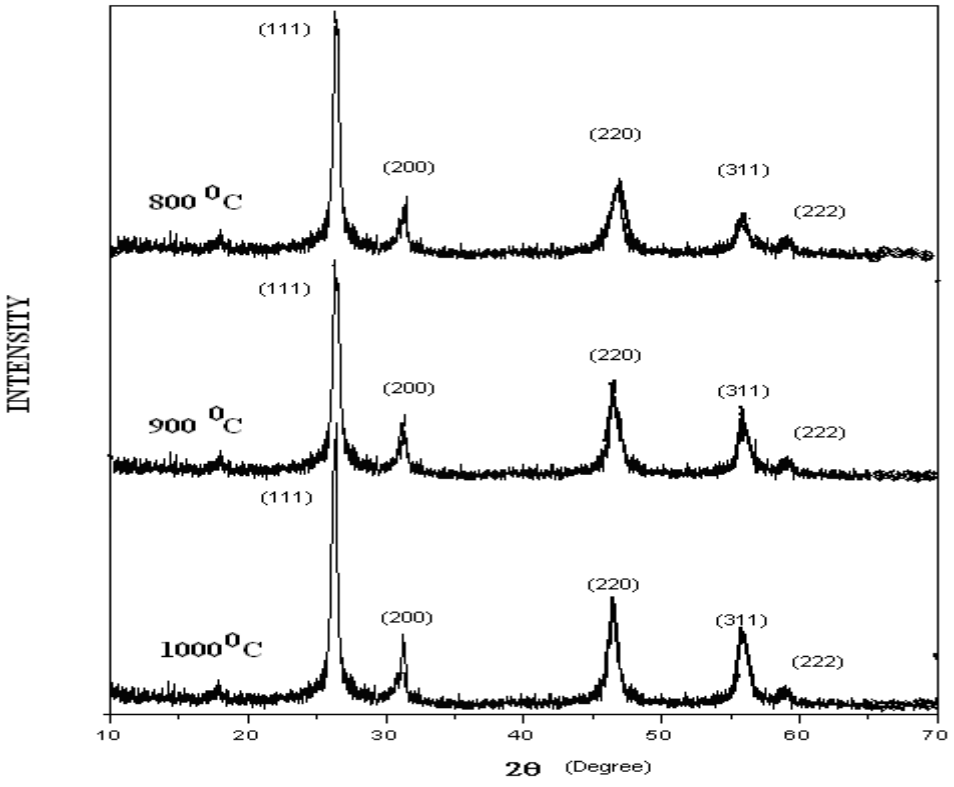


Fig. 1. XRD Pattern of ZrO_2 films at different firing temperatures.

In all cases, the observed peaks (111), (200), (220), (311) and (222) showed the presence of ZrO_2, match well with reported JCPDS data for confirming polycrystalline structure of the film. It has been observed that the XRD peak broadening decreases with an increase of the firing temperature. The intensity of reflections increases with a rise in the firing temperature. Also XRD analysis evaluates the

grain size of the thick films as function of the temperature. From this analysis all films were shown random orientation of polycrystalline nature of the material. The most pronounced and strongly reflected peak (111) was observed at 28 º. Also for further elevated temperature surface area decreases as grain size increases hence sensitivity decreases [23, 28]. In the field of chemical sensors, the structural stability, porosity and high surface to volume ratio are key properties for a sensing film [29].

Crystallite size or Grain size (D)

The XRD pattern was used to calculate the crystallite size of ZrO_2 by using equation-1 (Scherrer's formula) [22]. The crystallite size of ZrO_2 films at different firing temperatures is given in Table 2. The crystallite size of the film was found to be increase with an increase of the firing temperature as shown in Fig. 2.

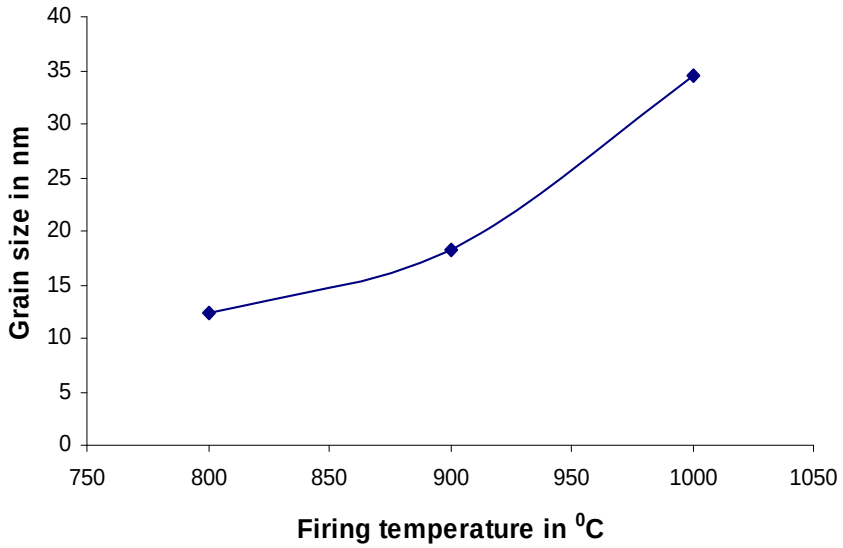


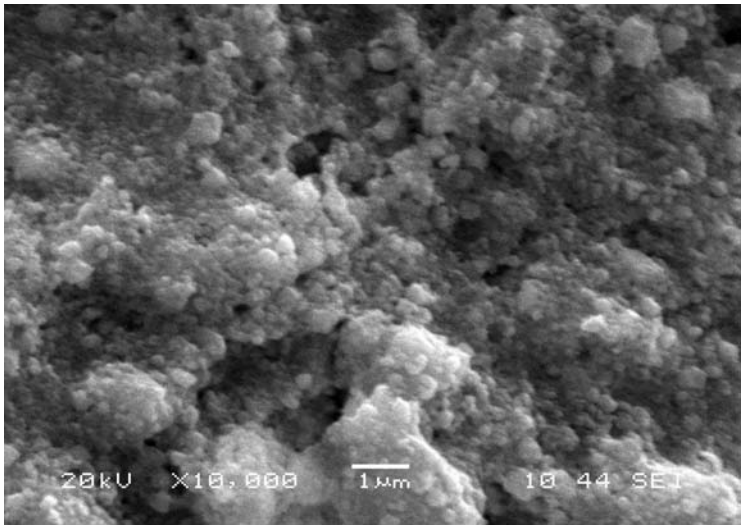
Fig. 2. Variation in crystallite size with temperature.

3.3.4. Surface Morphology Analysis

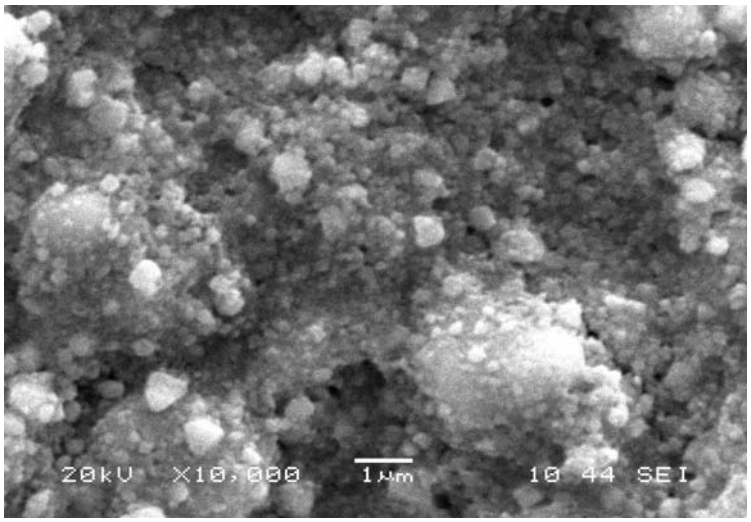
Fig.3 (a), (b) and (c) represents the SEM images of ZrO_2 Thick films fired at 800, 900 and 1000 ^{0}C respectively. All the images are recorded at 10,000x magnification for the comparison. The SEM pictures clearly shown that the crystallite size increases with an increase in the firing temperature. Surface morphology has shown the particle sizes are the function of the temperature.

It has been observed that an increase in the firing temperature leads to an increase in the crystallite size and decrease in surface area. The loss in surface area available upon elevated heat treatment would affect the sensitivity [30, 31].

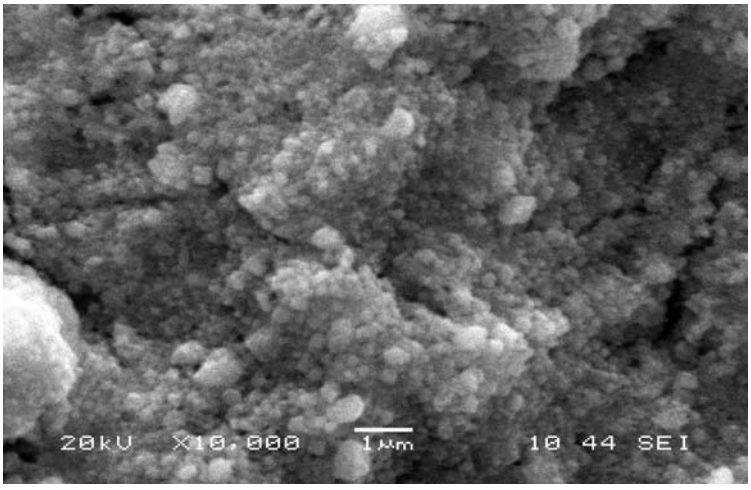
The specific surface area increases as the size of the grains decreases. It was measured by the BET by using equation-2 [23]. The particle size increases with an increase in the firing temperature hence specific surface area decreases. Normally, the smaller its grain size, specific surface area and oxygen adsorption quantity, the higher its gas sensitivity. The sensing properties of materials always benefit from the large specific surface area, which can improve the interaction between oxygen and material surface [31]. The surface area of ZrO_2 films at different firing temperatures is shown in Table 2.



(a)



(b)



(c)

Fig. 3. Scanning Electron Micrograms of ZrO_2 thick film samples fired at (a) 800 (b) 900 and (c) 1000 ^{0}C.

Table 2. Microstructural Parameters of ZrO_2 films fired at different temperatures.

Firing Temp. (^{0}C)	**Crystallite (Grain)Size((D) (nm)**	**Particle Size (nm)**	**Surface Area(Sw) m^2/g**
800	12.34	250	4.00
900	18.17	300	3.33
1000	34.42	400	2.50

4 Conclusions

ZrO_2 thick films were prepared on alumina substrate by standard screen printing technique which is simple and an inexpensive method. From EDS and SEM it was confirmed that ZrO_2 films were non-stotiometric, which are suitable for gas sensing application. The films fired in the temperature range of 800–1000 ^{0}C, were found polycrystalline. The grain size increases with an increase in the firing temperature hence specific surface area decreases. Film fired at 900 ^{0}C observed optimum surface area than further elevated temperatures. Film fired at 900 ^{0}C was shown more crystalline, porous, oxygen deficient, optimum specific surface area and good adhesion to alumina substrate. The film fired at this temperature may be suitable candidate for sensing applications. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of the films.

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